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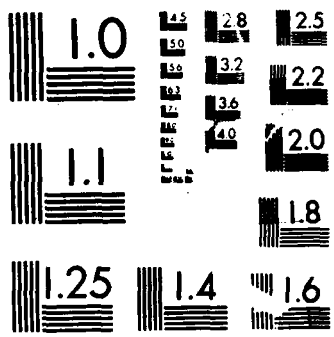

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Investigations of both macroscopic and microscopic properties of thin film superconducting materials have been carried out. Compounds under study prior to the discovery of high-T_c superconductors, were either technologically significant, or involved possible unique mechanisms for superconductivity whose realization might extend the range of critical parameters. These included low carrier density superconductors, selected Heavy Fermion Compounds, and Chevrel Phase superconductors. Among the low-carrier density systems were films of PbTe(Tl) and mixtures of La_2S_3 and La_3S_4. These were prepared with the idea of ultimately fabricating FET-like devices. Films of the Heavy Fermion Compounds UPt_3 and UBe_{13} were prepared and the critical fields and proximity effects in the latter were studied. With the advent of the high-T_c materials the program shifted to their study and measurements of their time-dependent magnetization, XPS spectra, and tunneling spectra were carried out on both bulk and thin-film materials.

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SUMMARY

Microscopic as well as macroscopic properties of selected thin film superconducting compounds, and high-T_c films and bulk material have been investigated. The particular materials under study prior to the discovery of superconductivity at elevated temperatures were either important for some aspect of superconducting electronics, such as the implementation of a superconducting FET, or involved possible unique mechanisms for superconductivity whose realization might have extended the know range of critical temperatures or critical magnetic fields upward.

Under study were two types of low-carrier-density-superconductors, Tl doped PbTe and La_2S_3-La_3S_4 mixtures. The intent was to fabricate a superconducting FET based on the metal field effect. Such a device would have three terminals, would exhibit input-output isolation and gain. The films of PbTe(Tl) were grown by molecular beam epitaxy (MBE) in collaboration with Dr. Dale Partin of GM Research Laboratories. The lanthanum sulfide compound films were grown using a multi-source E-Beam evaporation system which contained a combination of electron gun sources and Knudsen cells or molecular beam sources. With the discovery of high-T_c superconductivity, work on these materials was curtailed, and the results written up for publication. The idea of fabricating a superconducting FET is probably realizable with the new high-T_c superconducting materials and has become a goal of our new AFOSR-funded program.

Films of the heavy fermion compound UPt_3 had been fabricated using dc sputtering in year-two of this program. Although they evidently exhibited a degree of perfection they were not particularly good superconductors. The same technology was employed in year-three to grow films of UBe_{13}. These,

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although less perfect than the films of UPt_3, exhibited superconducting properties close to those of bulk polycrystalline material. Studies of the critical magnetic fields and proximity effects in these materials suggest that the pairing, at least near the surfaces which are the regions probed by such studies, is mostly s-wave in character in contrast with commonly-held beliefs. Measurements of critical magnetic fields which required fields of 22 Tesla and low temperatures were carried out using the facilities of the Francis Bitter National Magnet Laboratory in collaboration with James Brooks of Boston University.

With the discovery of the high-T_c layered Perovskite superconductors the research program described in this report was re-oriented. The major thrust became the fabrication and study of thin films and thin film structures of $YBa_2Cu_3O_7$ and related compounds. This is under way and is currently funded by the AFOSR. During the transition period several studies of the properties of the bulk material were undertaken and have been continued. These include the investigation of the time-dependence of the magnetization, studies of X-ray photoelectron spectroscopy, in particular its temperature dependence, and scanning tunneling microscope studies of both bulk and single-crystal samples of $YBa_2Cu_3O_7$. An account of the magnetization studies was submitted to Physical Review Letters in August before the end of this grant. The work involving XPS will be submitted shortly, and the tunneling investigations are at a more preliminary stage of their development.

Annual Technical Report

Superconductivity of Thin Film Intermetallic Compounds

Grant No. AFOSR-84-0347

September 15, 1987

School of Physics and Astronomy
University of Minnesota
Minneapolis, Minnesota 55455

Principal Investigator: Allen M. Goldman

TABLE OF CONTENTS

I. INTRODUCTION

The investigation of thin-film superconducting compounds is an important tool in furthering fundamental understanding of superconductivity. Also superconductors in the form of thin films are very important for many technological applications of superconductivity, both in superconductive electronics and in large-scale applications. In the matter of fundamental studies, the thin film geometry is useful in the characterization of both macroscopic superconductive properties such as critical magnetic fields, critical currents and critical temperatures as well as for studying microscopic properties such as the electron-phonon spectral function or other spectral functions that might be obtained using tunneling as a probe. With the introduction of ultra-high vacuum thin film fabrication techniques into the processing of compounds, the promise of better materials with higher critical temperatures and critical magnetic fields for large scale devices, as well as better-controlled device geometries for electronic applications may indeed be fulfilled. A unique feature of research in this field is that the development of technology at a level adequate to carry out fundamental scientific studies often facilitates the applications.

The above considerations are even more relevant within the context of the new superconducting materials such as $YBa_2Cu_3O_7$ and related compounds which have superconducting transition temperatures above 90K. These materials have rekindled broad interest in the applications of superconductivity and superconducting devices and at the same time represent a serious problem of a fundamental type, the illucidation of the mechanism for the high transition temperatures. Thus many of the ideas and proooblems

articulated earlier in the context of this program could be rather easily reconfigured to meet the new circumstances following the discovery of the new high-T_c materials.

This report will describe progress during the third year of a program of research on thin film superconducting compounds which began 1 September 1984. The effort was focussed on the fabrication of compounds employing techniques such as dc sputtering and electron beam co-evaporation. Materials which were studied included several low-carrier density superconductors, heavy fermion compounds, and superconducting Chevrel phase compounds. The focus has now shifted entirely to the new high-T_c materials.

A crucial aspect of the work is the correlation of microscopic and macroscopic superconducting parameters with composition and structure. Only by doing this can a detailed understanding of specific properties emerge. Microscopic properties were studied using electron tunneling and the usual macroscopic properties such as the critical current, critical magnetic field and critical temperature are also measured. X-ray diffraction analysis (XRD) is the primary tool in determining structure and identifying phases. Auger electron spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS), and electron microprobe analysis are also used in the work. A superconducting susceptometer has been used for magnetic investigations. Morphologies of films have been investigated using both scanning electron microscopy (SEM) and transmission electron microsopy (TEM). A scanning tunneling microscope (STM) is being used for both morphological and spectroscopic study of superconducting materials.

The fundamental scientific studies conducted under this program involve materials efforts which are intimately related to those needed for the

development of superconducting technology. Frequently the problem which must be solved to optimize the properties of a film for scientific study is the same as that encountered when the material or a related one is to be optimized for use as a conductor or in an electromagnet. Also the problems solved in preparing high-quality tunneling junctions for credible spectroscopic studies are closely related to the processing problems that must be solved in the preparation of tunneling devices for superconductive electronics.

II. PROGRESS

A. Facilities

Facilities development was not supported by grant funds during the past year. The work carried out under the grant employed facilities which included two DC sputtering systems, and one multi-source E-beam evaporator for the production of samples. Physical studies such as the investigation of the temperature dependences of the magnetization and resistance were carried out using a Quantum Design superconducting susceptometer, and a ^{3}He-^{4}He Dilution Refrigerator equipped with a 7.0 T superconducting magnet and a SQUID for magnetic studies at low temperatures. Measurements requiring ultra-high magnetic fields and low temperatures were carried out using the facilities of the Francis Bitter National Magnet Laboratory in Cambridge, Massachusetts.

B. Low-Carrier-Density Superconductors and the Superconducting Field Effect

This work was motivated by the prospect of using low-carrier density superconductors to fabricate three-terminal devices using the field effect. In such a device the carrier concentration in a superconducting layer would be changed by biasing a gate. This in turn would bring about a change in the superconducting transition temperature of the layer. If a three-terminal superconducting switch with isolation, high-speed, low-power dissipation and gain could be developed, the advantages of superconducting digital electronic relative to semiconductor electronics in the areas of power dissipation, packing density and ease of interconnection might be realized in a practical manner. Also such a superconducting transistor-like device could have applications in small scale superconductive electronics.

Towards this goal two types of superconducting compounds were studied, PbTe doped with Tl, first reported to be superconducting in the Soviet literature,[1] and La chalcogenides of the Th_3P_4 type, in particular the La_xS_y system.[2,3] With the discovery of the new High-T_c superconductors work on both of these compounds was terminated. Results were written up and have been accepted for publication. The work on PbTe(Tl) was published in Physical Review[4] and that on the lanthanum-sulfur system will appear shortly in Thin Solid Films.[5]

The work on the PbTe(Tl) system involved a collaboration with Dr. Dale Partin of the General Motors Research Laboratory. This collaboration has been terminated. The effort on the lanthanum sulfur system was carried out using the multi-source E-beam evaporation system. With the cessation of this effort that system was cleaned up and dedicated to the growth of films of $YBda_2Cu_3O_7$. These efforts will be described in a subsequent section of this report.

C. Heavy Fermion Compounds

These materials have been studied extensively because of the remarkable fact that their electron effect masses can be as large as 1000 times that of the free electron mass.[6] The cause of these large effective masses is in of itself an unresolved puzzle which raises a number of interesting questions which relate to the nature of the superconductivity of these compounds. It is very hard to understand how the usual mechanism for superconductivity can be valid in a system in which the characteristic lattice energies are actually larger than the electronic energies. The retarded electron-phonon interaction must be substantially modified under such circumstances. It is believed that more purely electronic effects are responsible for superconductivity in these materials, than the conventional electron-phonon interaction. The heavy fermion compounds are also believed to involve pairing with higher spin and angular momentum that is the case for the usual BCS superconductors which contain singlet pairs with zero orbital angular momentum.

During the past year we ceased our efforts at producing UPt_3 films and concentrated on UBe_{13} films. The latter were much easier to grown in pure form because they required much lower substrate temperatures and because UBe_{13} is the only compound in the U-Be phase diagram. The method used for both kinds of films was DC sputtering. The very first, and all subsequent efforts at producing UBe_{13} films were successful, with X-ray patterns and macroscopic superconducting properties both very close to those of bulk material.[7]

Attempts to produce tunneling junctions on UBe_{13} films and on proximity sandwiches of UBe_{13} and Al were not successful although many intriguing and

suggestive tunneling characteristics were observed during the course of the work. Failing to produce tunneling junctions in these configurations, we concentrated on studying the properties of proximity sandwiches and of the thin films themselves. In the case of the films, we studied the parallel and perpendicular critical magnetic fields. Such measurements can be used to understand the nature of surface superconductivity in these materials.[8] The work on the proximity effect was directed at determining whether there was a negative proximity effect.[9] This phenomenon was predicted theoretically for the case of a film of heavy fermion compound which exhibited triplet pairing in proximity with a film of a conventional s-wave or singlet superconductor. In the case of a negative proximity effect, the onset of superconductivity in the triplet layer would suppress or reduce that of the singlet material. There has actually been a report of this phenomenon in experiments involving point contact tunneling.[10] The latter work has been criticized by us in a Comment in Physical Review Letters.[11] The results of both of our experimental studies on UBe_{13} films are consistent with the presence of singlet pairing at least at the surface of the film, a result in conflict with widely held, but not necessarily correct views of the nature of pairing in this material.

Typical UBe_{13} films were 3000Å thick and were deposited onto single-crystal sapphire substrates. The temperature dependences of the parallel and perpendicular critical fields were determined resistively. The ration $H_{c\parallel}/H_{c\perp}$ was found to be 1.25, a value which suggests the partial rather than the complete suppression of surface superconductivity of the films. This result is believed to imply that the pairing configuration in UBe_{13}, at least near the surface cannot be pure triplet or any other pure

state with $L \neq 0$. An account of this work will appear in the Proceedings of the Eighteenth International Conference on Low Temperature Physics,[12] and in the Proceedings of the Berkeley meeting on Novel Mechanisms of Superconductivity.[13]

In the case of the measurements on the proximity effect, the critical fields of sandwiches of 3000Å thick films of UBe_{13} with films of Al of various thickness were measured. When the heavy fermion film was in intimate contact with the Al film, an enhancement of the critical field was observed at the onset of superconductivity of the heavy fermion compound. This result is inconsistent with the occurrence of a negative proximity effect and probably rules out higher angular momentum pairing at least at the surface of the heavy fermion compound. The measurements are a little different from the usual proximity effect experiments in that rather than studying how superconductivity is induced in a normal metal in proximity with a superconductor, they are directed at probing how superconductivity is enhanced or suppressed by the onset of superconductivity in a normal layer. In this instance the normal layer has a much higher critical magnetic field, but much lower transition temperature than the superconducting layer.

The results mentioned above are described in detail in the Doctoral Dissertation of Dr. J. Kang, who recently joined the staff of Argonne National Laboratory as a Post-doc. It is planned to write up a short paper on the proximity effect and submit it for publication in Physical Review Letters in the near future. Research in this area has terminated with the departure of Dr. Kang.

D. High-T_c Superconductivity

The discovery of superconductivity at temperatures above the atmospheric boiling temperature of liquid nitrogen was the major scientific event of the last year.[14] This event forced the re-direction of the resources of many programs of research on superconducting materials including this one. The renewal of the present grant is devoted entirely to the study of high temperature superconductivity. Work on high temperature superconductors was directed at a number of problems. These include the measurement of the time-dependent magnetic properties of bulk $YBa_2Cu_3O_7$, scanning tunneling microscope studies of this compound, investigations of the temperature dependence of X-ray photoelectron spectroscopy of core levels, and work on the growth of thin films produced using both E-beam co-deposition and magnetron sputtering. Here we will describe the magnetic studies, the research employing a scanning tunneling microscope, and the work on thin films. The other efforts were not sufficiently far along at the end of the grant period to represent significant accomplishments for the purposes of this report.

The studies of the time-dependent magnetization of grew out of an effort to determine whether there was a phase diagram for $YBa_2Cu_3O_7$ similar to that of the superconducting glass proposed by Muller and co-workers[15] as an explanation of their measurements on one of the K_2NiF_4 compounds which have superconducting transitions in the range from 30 to 40K. The time dependence of the magnetization was studied in order to ascertain the limits of the glass-like state. Remarkably slow rates of decay were found to persist and to continuously decrease with increasing temperature up to the superconducting transition. This result suggest that the latter is the

through the temperature dependence of the decay rates. At very low temperatures we observe a rate of decay which increases with increasing temperature. The rate achieves a maximum at about 30K above which it decreases with further warming. It is our belief that the glass-like state is relevant only above 30K where the decay rate slows down with increasing temperature, and that the low temperature behavior can be described as flux creep of Abrikosov vortices.

An account of this work has been prepared and submitted for publication in Physical Review Letters.[16] A reply from the referees is expected shortly.

We have also undertaken tunneling studies of the high temperature superconductors using scanning tunneling microscopy (STM). The initial work, which will be described here, employed polycrystalline bulk samples of $YBa_2Cu_3O_7$. Efforts which will be described in subsequent reports were directed at the study of single-crystal material. In the work of the bulk material we were never able to observe topographical features of the surface of the material. The energy gap could be seen only if the tip were physically stuck into the surface. Gaps ranging in value from 20 to 60 mV were observed in an essentially random manner. In measurements at room temperature and at voltages out to 1.2 V features were observed at 120 mV and 500 mV. These anomalies may be related to the structure observed in infra-red absorption measurements at 0.5meV [17] which have been ascribed to either excitons or polarons, depending upon the particular prejudices of the experimenter or the theorist commenting on the observations. A report of these anomalies has not been made as they could not be clearly associated with superconductivity. The interpretation of STM results in bulk

these anomalies has not been made as they could not be clearly associated with superconductivity. The interpretation of STM results in bulk polycrystalline samples of the high temperature superconductors is difficult because of the poor quality of the surfaces of these materials. We will probably never report results on these materials obtained using STM, but are pursuing similar investigations using single-crystal material and hope to report our new finds in the near future. Preliminary work on single-crystal material indicates that we are resolving surface atomic features.

Our work on thin films is fully under way. We converted our E-beam evaporation system to the production of thin films of the high-T_c materials, and purchased a quantity of single-crystal $SrTiO_3$ substrates which are apparently necessary to obtain the best results. We have calibrated rates using X-ray diffraction analysis (XRD) and energy dispersive X-ray analysis (EDX) to obtain compositions and phases. Our preliminary results indicated substantial drops in electrical resistance near 100K with the completion of the superconducting transition in the range from 40-60K. Empirical variations of annealing conditions are under way and we expect to be able to continue to improve the quality of our films with further work, and achieve films of qualities comparable to those which have been attained at other laboratories.

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III. PUBLICATIONS AND REPORTS

A. Publications

1. Time-Dependent Magnetization of a Superconducting Glass, by M. Tuominen, A.M. Goldman, and M.L. Mecartney, submitted to Physical Review Letters.

2. Comment on "Observation of Negative s-Wave Proximity Effect in Superconducting UBe_{13}", by A.M. Kadin and A.M Goldman, Phys. Rev. Lett. 58, 2275 (1987).

3. Superconductivity in the ferromagnetic phase of polycrystalline $HoMo_6S_8$ Films, by J. Maps, D.D. Berkley, J.H. Kang, and A.M. Goldman, Phys. Rev. B. 35, 38 (1987).

4. Critical Fields of UBe_{13} Films, by J.H. Kang, J. Maps, A.M. Goldman, J.S. Brooks, Z. Fisk, and J.L. Smith, in Proceedings of the International Workshop on NOVEL SUPERCONDUCTIVITY, Berkeley, California, June 22-26, 1987, Edited by Stuart Wolf and Vladimir Z. Kresin, Plenum Press, New York, (1987), p. 215-221.

5. Superconductivity in Thin Films of UBe_{13}, by J.H. Kang, J. Maps, A.M. Goldman, J.S. Brooks, Z. Fisk, and James L. Smith, to be published in the Proceedings of the Eighteenth International Conference on Low Temperature Physics.

6. Superconducting Transition in Thin Films of Lead Telluride Doped with Thallium, by J.H. Kang, J. Maps, D.D. Berkley, H.M. Jaeger, A.M. Goldman, and Dale L. Partin, Phys. Rev. B 36, 2280 (1987).

7. Vapor-Deposited Superconducting Lanthanum Sulfide Films, by D.D. Berkley, J.H. Kang, J. Maps, J.-C. Wan, and A.M. Goldman, to be published in Thin Solid Films.

B. Reports

1. Superconductivity in Thin films of the Heavy Fermion Superconductors, UPt_3 and UBe_{13}, by Joonhee Kang, Doctoral Dissertation, University of Minnesota, September 1987.
2. Superconductivity in Thin films of Heavy Fermion Compounds, by J. Kang, J. Maps, A.M. Goldman, Z. Fisk and J.L. Smith, Bull. Am. Phys. Soc. 32, 684 (1987).
3. Vapor-Deposited Superconducting Lanthanum Sulfide Films, by D.D. Berkley, J. Kang, J. Maps, J.-C. Wan, and A.M. Goldman, Bull. Am. Phys. Soc. 32, 689 (1987).
4. Superconductivity of PBTe:Tl films Grown by Molecular Beam Epitaxy, by J. Maps, J. Kang, D. Berkley, H.M. Jaeger, A.M. Goldman, and Dale L. Partin, Bull. Am. Phys. Soc. 32, 689 (1987).
5. Superconductivity of Thin Films of UPt_3 and UBe_{13}, by Joonhee Kang, Doctoral Dissertation, Sept. 1987.

IV. PERSONNEL

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APPENDIX

Time-Dependent Magnetization of a Superconducting Glass

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ABSTRACT

The time dependence of the magnetization of polycrystalline samples of the high temperature superconductor $YBa_2Cu_3O_7$ has been investigated in order to ascertain the limits of the glass-like state. Slow rates of decay have been found to persist and to continuously decrease with increasing temperature up to the superconducting transition, suggesting that the latter is the upper bound on glass-like behavior.

The concept of glass-like behavior of superconductors was first discussed a number of years ago by Hertz[1] who treated a continuum model with a random field. More recently, Stroud and co-workers[2] in a series of papers pointed out that the application of a magnetic field to a granular superconducting material would introduce frustration[3] into the Josephson coupling between grains[4] and showed, using Monte Carlo techniques, that this would lead to behavior analogous to that of spin glasses. A randomly diluted lattice of Josephson junctions was found to be a glass in the analytical model given by John and Lubensky.[5] Glass-like properties were also found theoretically for regular 2-D Josephson-junction arrays, in certain magnetic fields.[6] Experimental evidence for the existence of a superconductive glass state was presented by Muller, Takashige and Bednorz[7] (MTB) who inferred its existence from measurements of the susceptibility and magnetic moments of the high-T_c superconductor La-Ba-Cu-O. Similar conclusions relating to the glass-like behavior of the same system were reached by Razavi _et al_.[8] and for $YBa_2Cu_3O_{7-\delta}$ by Carolan _et al_.[9]

In this letter we present the results of detailed measurements of the temperature dependence of the decay of the magnetization of bulk polycrystalline samples of the high temperature superconductor $YBa_2Cu_3O_7$. We find many of the features of the so-called superconducting glass state reported by MTB, but the more extensive nature of our measurements of the decay of the magnetization leads us to somewhat different conclusions relating to the phase diagram. In particular, the locus of points denoting the intersection of the field-cooled and zero-field cooled magnetizations which MTB have identified as the de Almeida-Thouless line[10] is not found to be a relevant boundary. A major feature of our measurements is that we are

able to exclude conventional flux creep[11] as an explanation of the nonexponential time dependences of the magnetization over a substantial range of temperatures. Furthermore, if the glass phase is defined by the occurrence of long-time nonexponential decays of the magnetization, then we would conclude that the glass transition and the superconducting transition in the magnetic field are essentially indistinguishable. In contrast with conventional spin glasses where long decay times are a low temperature property, the decay times appear to diverge as the superconducting transition is approached from below. The time-dependence of the magnetic response above the superconducting transition temperature is that of a normal conductor.

Because these measurements have been carried out on polycrystalline aggregates the behavior can be attributed at this time to the granular structure of the material and should not be considered to be an intrinsic property of the high-T_c superconducting state as has been suggested in a number of theoretical models.[12-14] However, preliminary measurements on single crystals which may have twin boundaries have yielded results very similar to those reported here, lending support to the view expressed in Ref. 7 that the characteristic size of the "grains" is nearly microscopic and smaller than the actual crystallites. Only an extension of these studies to defect-free single crystal materials would establish the relevance of the present considerations to the intrinsic character of the superconducting state of high-T_c materials.

The $YBa_2Cu_3O_7$ samples were prepared using standard solid state reaction techniques[15] and determined to be the 1-2-3 phase by X-ray diffraction analysis. The existence of superconductivity was determined resistively

using a four-point method. The onset of the transition was at 93 K and zero resistance was achieved at 90 K. The data reported in detail here was obtained using a sample which had a mass of 0.070 g, and dimensions of 1.1mm x 1.9mm x 9.0mm. Scanning electron microscope analysis revealed a structure which consisted of elongated irregular plates with characteristic lengths of 10 to 20 μm and widths of 2 to 5 μm. Magnetic measurements were performed using a SQUID susceptometer.[16] All temperature values reported were determined using calibrated carbon glass and platinum resistance thermometers provided with the susceptometer. The long axis of the sample was always aligned in the direction of the magnetic field, a configuration in which the demagnetizing factor was 0.05.

Field cooled (FC) and zero field cooled (ZFC) magnetization measurements were made in fields ranging from 50 to 5000 G. Representative data is shown in Fig. 1 and is similar to behavior reported by MTB.[7] The data was obtained by first cooling the sample in zero field to 5 K, and then switching on a magnetic field and measuring the magnetization as a function of increasing temperature up through the value of T_c for the material. Then the sample was cooled in a field and the magnetization was again measured while warming. A typical temperature sweep took three hours. The ZFC and FC curves intersect at a temperature MTB[7] called T*.

A difference between the ZFC and FC magnetizations is one of the salient features of a magnetic spin glass. Similar behavior would be expected of a phase glass or superconducting glass. Because the FC curves are reversible and the ZFC are not, T*, the temperature at their intersection has been identified by MTB[7] as the temperature demarking the boundary between ergodic and non-ergodic behavior. The boundary, or quasi

de Almeida-Thouless line,[16] was given by $T^* = T_c[1-(H/H_0)^{1/\gamma}]$. The present data is similar to that of MTB[7] in this instance, with $H_0 = 7600$ G, $T_c = 90$ K and $\gamma \sim 1.5$. However, as the ZFC and FC curves join tangentially, T* is really not well-defined.

It should be noted that for a disordered and porous superconductor one might expect different magnetizations for the ZFC and FC cases simply because of different roles played by the Meissner effect and dc screening.[17] Consequently the proof of glass-like behavior would appear to depend upon the observation of nonexponential time decays in the magnetization when the external magnetic field is changed abruptly. Such decays were indeed observed by MTB[7], and were cited as evidence for the glass-like character of the superconductivity. A difficulty with this is that there is another phenomenon associated with Type-II superconductors, known as flux creep, in which trapped flux is also known to decay in a nonexponential fashion.[11]

Detailed studies of the dynamics have been carried out by measuring the decay of flux trapped in the sample as a function of time. This is in analogy to the thermoremnant magnetization in spin glasses. The sample was systematically cooled in a 500 G field to the temperature of interest, thereby introducing flux into the material. The applied field was then switched off. The magnetic response in the field quickly switched sign and the remaining trapped flux (paramagnetic signal) was found to decay linearly in ln(t) in a manner similar to remnant decay in spin glasses. Decays as a function of time at several temperatures are shown in Fig. 2.

Since the rate of decay is dependent on the magnitude of the trapped flux, each decay line should be normalized by dividing the rate by the magnitude of the initial trapped flux. In Fig. 3 we present the normalized

rates of decay. M_0 corresponds to the flux trapped at t = 1 min. It should be noted that the normalized decay rate continues to decrease as T_c is approached from below and there is no discernible change going through T*. These results suggest that the transition to glass-like behavior actually begins at $T_c(H)$ and not at T*.[5] The measurements actually raise serious questions as to whether an equilibrium phase diagram of the type implied by Fig. 1 has meaning unless measurements are carried out over extremely long times.

It is important to note that there is a peak in the temperature dependence of the decay rate at about 30 K. Below this temperature the rate of decay increases with T, behavior consistent with both flux creep and the decay of the magnetization in real spin glasses. The observed continuing decrease of the rate with temperature above 30 K as the superconducting transition is approached from below suggests a kind of critical slowing down which, to our knowledge, is not contained in any model of either the spin glasses or the superconducting glass. The decay of the magnetization cannot be described as flux creep, the rate of which would increase with T.

Also suggestive of a glass-like state is our observation of the predicted instability of the ZFC curve.[2] Measuring the magnetization of points on this curve as a function of time, we have found them to decay linearly in ln(t) towards the FC curve which is itself stable in time. The rate of this ZFC decay is also temperature dependent and has a maximum at 30 K in a field of 500 G. As the field is increased there is a decrease in the temperature at which the maximum is found. For the particular sample reported here, it shifts down to 5 K when the field is increased to 5000 G.

It should be noted that results similar to those described above have also been found for samples with different densities and processing histories and as mentioned above even in single crystals. The behavior is the same from sample to sample although the details of the transition temperatures and temperatures of the maximum in the decay rate did vary somewhat.

Although there are many formal similarities between spin glasses and the superconducting glass, it is important to realize in interpreting these data that there are differences which greatly weaken the analogy as the measured magnetizations are related to the underlying order parameters in rather different ways. In a spin glass, the magnetization is directly related to the Edwards-Anderson[18] order parameter, whereas in the superconducting case it depends on macroscopic circulating currents which in turn depend on spatial gradients of the phase of the local order parameter. Furthermore, the magnetic field is the thermodynamic conjugate field to the magnetization in magnetic systems in which the tendency is towards ferromagnetic ordering whereas in the superconducting case, where the intergrain coupling is ferromagnetic and X-Y like in character, the applied magnetic field is not the conjugate field.

In the case of the spin glass, the application of a field reduces the disorder in the system, tending to align the microscopic magnetic moments. However, in the superconducting case the field itself is the origin of the frustration in which some of the couplings are ferromagnetic whereas others tend to align pseudo-spins at angles other than zero degrees.

In summary, we have investigated the temperature dependence of the decay of magnetization in a granular superconductor. Nonexponential decays

with long time constants have been observed all the way up to the transition temperature. The decay rate is an increasing function of temperature at low temperatures up to about 30 K. Above this temperature the decay rate decreases with increasing temperature with rapid response being restored only above T_c. This is different from the recent results of Mota *et al.*[19] who report only an increase in $\partial M/\partial \ln t$ with T in Sr-La-Cu-O and Ba-La-Cu-O, both of which are superconductors with lower values of T_c. Our results are suggestive of a superconducting glass which is rather different from the simplest analogies with spin glasses. In particular, the phase diagram suggested by MBT would appear to be relevant only on short time scales.

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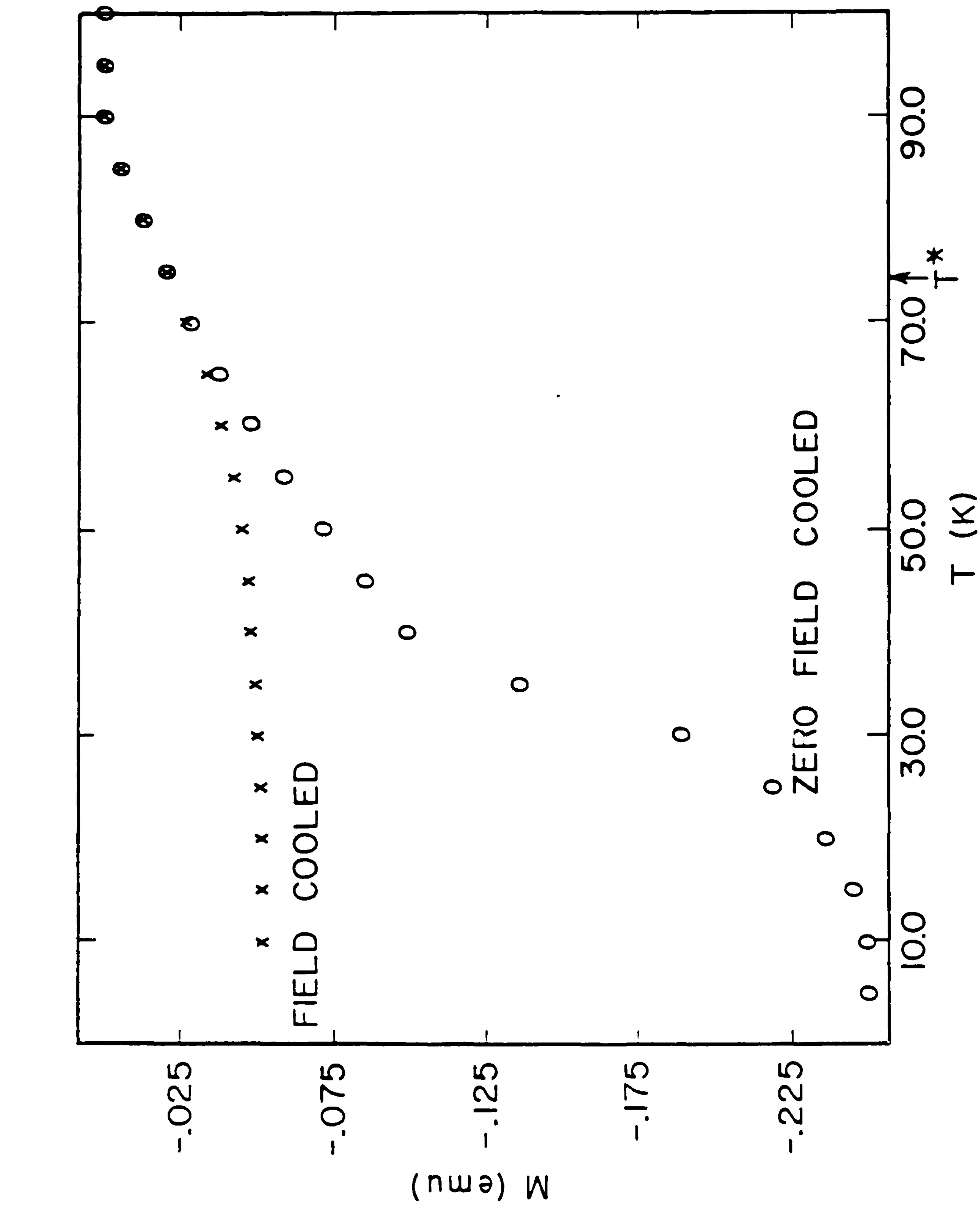
Figure Captions

Fig. 1. Field cooled and zero field cooled magnetization measurements of a $YBa_2Cu_3O_7$ sample taken using a field of 500 G.

Fig. 2. Magnetization vs. time of the sample studied in Fig. 1. Measurements were obtained by cooling in a field of 500 G and then removing the field. The residual magnetic field during these measurements was the order of 3 G.

Fig. 3. Temperature dependence of the fractional change of the magnetization. M_0 is the magnetization measured one minute after the removal of the external magnetic field.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-.075
-.125
-.175
-.225
T (K)
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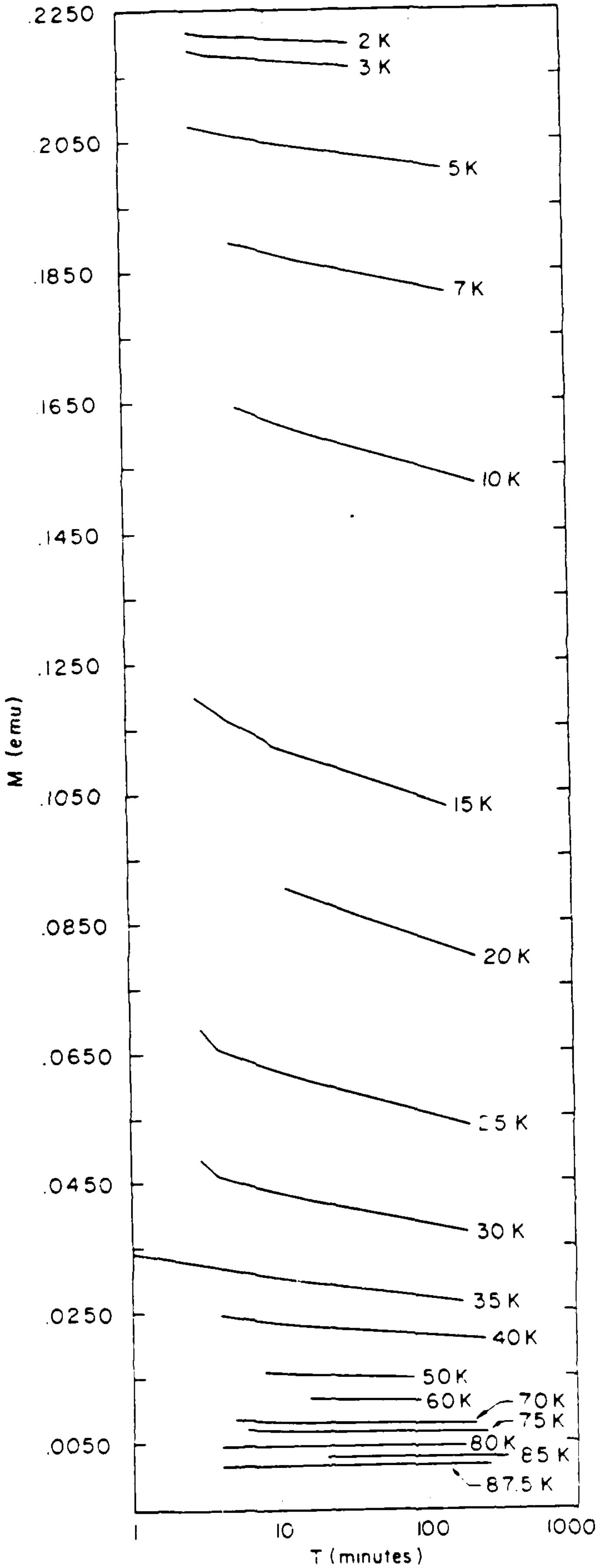
30.0
50.0
70.0
90.0
T*
FIELD COOLED
ZERO FIELD COOLED



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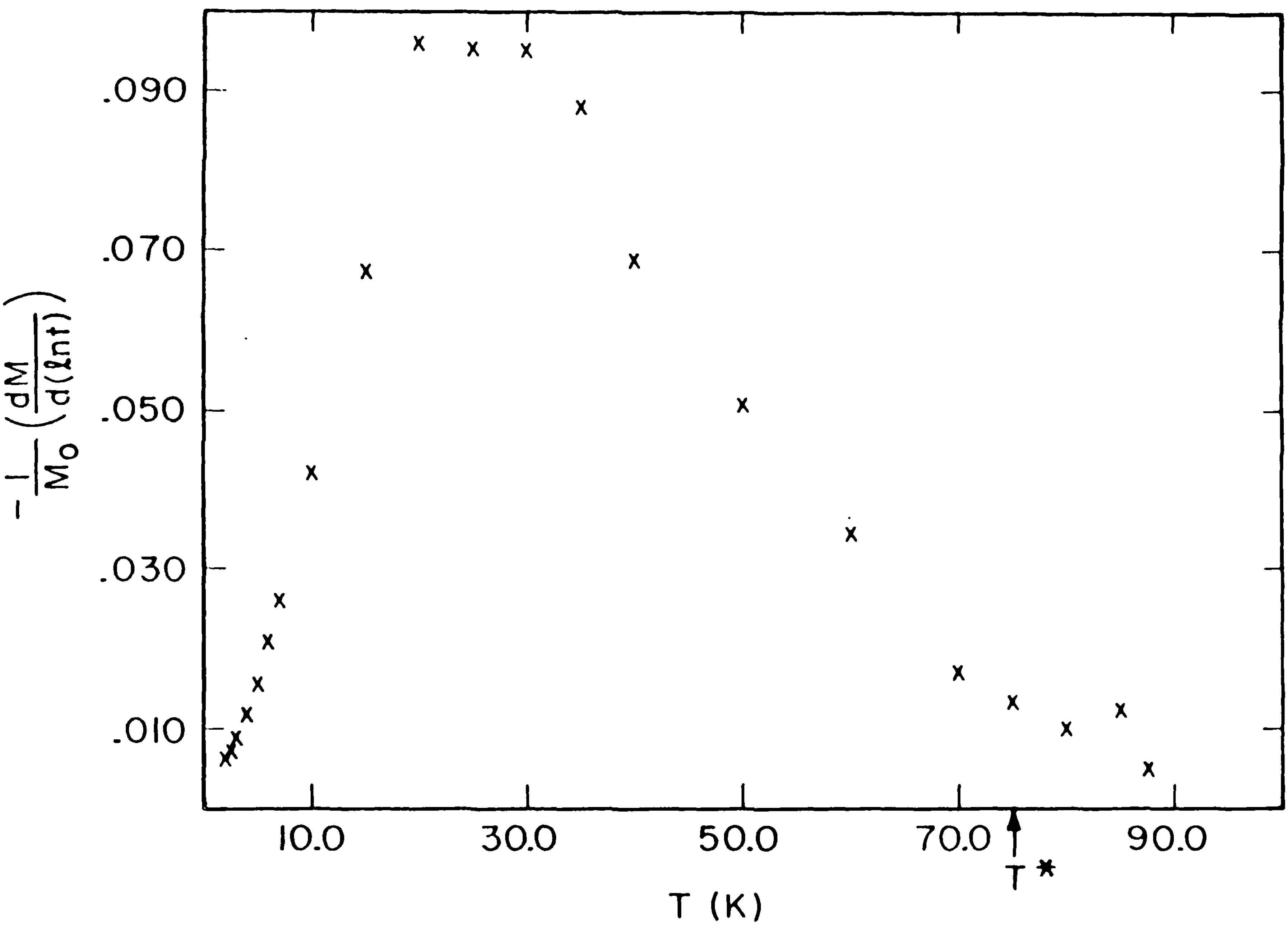
.2050
.1850
.1650
.1450
.1250
.1050
.0850
.0650
.0450
.0250
.0050
M (emu)
2 K
3 K
5 K
7 K
10 K
15 K
20 K
25 K
30 K
35 K
40 K
50 K
60 K
70 K
75 K
80 K
85 K
87.5 K
1
10
100
1000
T (minutes)


$-\frac{1}{M_o}\left(\frac{dM}{d(\ell n t)}\right)$
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.070
.050
.030
.010
10.0
30.0
50.0
70.0
90.0
T*
T (K)

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